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Kenneth J. Wynne

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Excited-State Complexes of Conjugated Polymers: Novel Photophysical Processes and
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Samson A. Jenekhe

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13. ABSTRACT (Maximum 200 words) Although the ground-state charge transfer complexes of π -conjugated polymers have been widely investigated in the past two decades, the corresponding excited-state complexes were only recently discovered. The results of our extensive studies of intermolecular excimers and exciplexes of many conjugated polymers will be presented in the talk. The observation of excimer and excimer emission of many conjugated polymers provides a new model of the photophysics of the materials. It will be shown that the modified Birks' mechanism of intermolecular excimers can explain all the essential features of the luminescence of conjugated polymers. The luminescence and charge photogeneration in exciplexes of conjugated polymers with donor triarylamines will also be presented.					
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Samson A. Jenekhe

Department of Chemical Engineering and Center for
Photoinduced Charge Transfer
University of Rochester
Rochester, New York 14627-0166

1. Introduction

The ground-state charge transfer complexes of π -conjugated polymers, better known as doped conducting polymers, have been widely studied since 1977 when their high dark electrical conductivity was discovered. A large number of conducting polymers with conductivities in the semiconducting to metallic range (10^{-7} to 10^5 S/cm) have been prepared from diverse π -conjugated polymers and dopants [1]. In contrast, excited-state complexes of π -conjugated polymers, including excimers and exciplexes, were only very recently discovered [2-4]. The study of these excited-state complexes of conjugated polymers holds promise for increasing our fundamental understanding of the photophysical and photochemical processes in conjugated polymers as well as optoelectronic materials with possible applications in light emitting diodes, xerographic photoreceptors, solar cells, and nonlinear optics, among others. Our studies of excimers and exciplexes of π -conjugated polymers will be discussed in this paper.

Intermolecular excimers and exciplexes in small molecules have been known and widely studied since 1954 and 1963, respectively [5-7]. These excited-state complexes have also been well known and investigated in vinyl polymers containing aromatic chromophores as side groups or as chain ends [5]. It may seem surprising then that such excited-state complexes were not explored in π -conjugated polymers until recently. However, the reason appears to be that until recently the photophysics and excited states of conjugated polymers were described largely in terms of a quasi-one-dimensional semiconductor band model [8] rather than in terms of molecular excitons [9]. Another important consideration is the prior neglect of interchain excited-state processes in conjugated polymers. That interchain excitations could be significant, and possibly dominant, is suggested by the morphology of π -conjugated polymers which shows very close (~ 3 -4 Å) face-to-face packing of relatively stiff and planar molecules [10]. Such a chromophore packing arrangement means that conjugated polymers are full of pre-existing intermolecular excimer-forming sites capable of forming excimers upon excitation. Also, since chromophores in π -conjugated polymers are well-known to function as either electron donors or acceptors in ground-state charge transfer reactions, they should also be capable of similar function in excited-state charge transfer reactions.

Intermolecular excimers and exciplexes of conjugated polymers have been extensively investigated in our laboratory by different approaches, including the synthetic approach of controlling interchromophore distances through copolymerization [11] and the study of blends of conjugated polymers with nonconjugated polymers, solutions, and bilayer thin films [2-4]. This paper will focus on the latter approach. The conjugated polymers we have studied are exemplified by the rigid-rod polymers poly(*p*-phenylene benzobisthiazole) (PBZT), poly(*p*-phenylene benzobisoxazole) (PBO), and poly(2,5-pyridyl benzobisthiazole) (PPyBT). These and related polymers form excimers efficiently as thin films whereas with tris(*p*-tolyl) amine (TTA) or other donors they form exciplexes. Our studies of these excited-state complexes of conjugated polymers are described in detail elsewhere [2-4, 11].

2. Experiments

The synthesis and characterization of the conjugated rigid-rod polymers have been reported previously. Thin films of the conjugated polymers or their blends with either poly(1,10-decamethylene benzobisthiazole) (PBTC10) or poly(methyl methacrylate) (PMMA) were prepared from solutions in nitromethane-aluminum trichloride. Thin films for spectroscopic measurements were spin coated onto glass or fused silica substrates. In the case of bilayers thin films, the conjugated polymer thin film layer was first deposited on a substrate and then a layer of poly(bisphenol A carbonate) containing 40 wt% TTA was deposited by either spincoating (samples for spectroscopic measurements) or blade coating

(samples for charge photogeneration studies) from a dichloromethane solution. Steady-state photoluminescence (PL) was measured on thin films, blends, and polymer solutions in methane sulfonic acid (MSA). Time resolved (ps) PL decay dynamics was done on all conjugated polymer thin films and selected bilayers, blends, and fluid solutions. The quantum yield and the mechanism of charge photogeneration were investigated by using the xerographic photoinduced discharge technique. All the photophysical measurements were made at room temperature and the details can be found elsewhere.

3. Results and Discussion

The photoluminescence emission spectra of thin films of conjugated rigid-rod polymers such as PBZT, PBO, or PPyBT were found to be generally broad and structureless. Such an emission spectrum is shown in Figure 1a for a thin film of PPyBT which has an emission λ_{max} at ~ 560 nm. The thin film PL emission spectrum ($\lambda_{\text{max}} = 450$ nm) of a PPyBT/PMMA blend ($\sim 10^{-3}$ mol% PPyBT) is shown in Figure 1b. A dramatic difference between the two emission spectra in Figure 1 is seen. First, there is a large blue shift of the blend emission from that of the pure conjugated polymer thin films. Second, the emission from the blend is highly structured, revealing vibronic structure in the emission spectrum. Third, the emission of the PPyBT/PMMA blend is significantly enhanced compared to the pure PPyBT thin film. These general features of the PL emission spectra of PPyBT and its blends with PMMA were also observed in many other conjugated polymers that we have studied. These results show that thin films of these conjugated polymers form excimers and that their luminescence is from excimer emission. Thus, the "single chromophore" or "single chain" emission (e.g. Figure 1b) of these conjugated polymers is observed only in the dilute blend or fluid solutions where the interchromophore/interchain distances are large. The time-resolved PL decay dynamics of thin films of all the conjugated polymers was generally nonexponential as exemplified by the PL decay dynamics of PBO thin film shown in Figure 2.

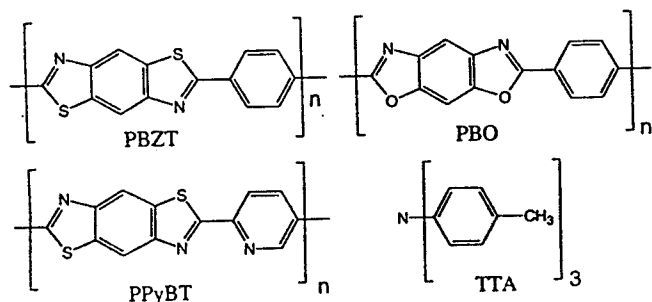
Our observations of excimers and excimer emission in many π -conjugated polymers provide a new basis for understanding the photophysics of π -conjugated polymers [2]. We find that Birks' classic kinetic model of intermolecular excimer formation, shown in Scheme 1, can be profitably applied to π -conjugated polymers. In this scheme, A^* is an excited (assumed to be a singlet excited state) chromophore on a conjugated polymer chain, A is an unexcited chromophore on an adjacent polymer chain, and the excimer formed is represented by $(AA)^*$. This simple excimer kinetic mechanism can qualitatively explain all the observed features of the steady-state and decay dynamics of the solid state luminescence of π -conjugated polymers. For example, the broad and often structureless PL spectra, the nonexponential PL decay dynamics, the large apparent Stokes shift between absorption and emission maxima, and the poor PL quantum yields of conjugated polymer thin films can be readily rationalized in terms of Scheme 1. However, a detailed quantitative description of the photophysics of conjugated polymers requires a more sophisticated view of the nature of the excited-state complexes or excimers. Since the chromophores in conjugated polymers have a distribution of size or conjugation lengths one can expect more than one excimer state, hence Scheme 1 must be modified: $A^* + A_j = \Sigma(A_i A_j)^*$. A quantitative description of the excimer emission decay dynamics of conjugated polymers such as in Figure 2 suggests at least two excimer states. In the case of the PBO decay dynamics in Figure 2, it was best fitted to a biexponential model with lifetimes of 50 ps and 660 ps.

The π -conjugated rigid-rod polymers such as PBO or PBZT are good excited-state electron acceptors (A) relative to the donor (D) triarylamine TTA. In the form of D/A blends or bilayers, we have found no spectroscopic evidence for ground-state interaction. However, upon photoexcitation, D/A exciplexes of the conjugated polymers are formed as a result of photoinduced electron transfer [2-4] as illustrated in Scheme 2. In the case of D/A bilayer thin films, the exciplex is formed at the interface within about 100 picosecond or less [4]. Exciplex formation leads to a significant modulation of the photophysical properties of the conjugated polymers, most notably the luminescence and charge photogeneration [2-4]. The large enhancement of the quantum yield for charge photogeneration upon exciplex formation has been exploited in xerographic photoreceptor devices [4]. Enhanced luminescence of the conjugated polymer exciplexes has potential application in electroluminescent diodes. It is also expected

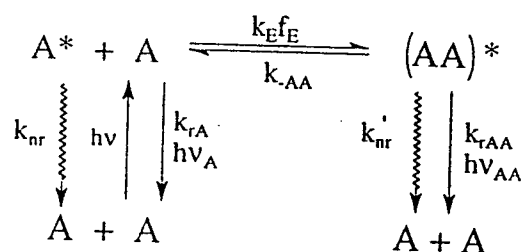
that the nonlinear optical properties of conjugated polymers could be significantly enhanced by exciplex formation owing to the excited-state dipole moment and new optical paths.

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Scheme 1



Scheme 2

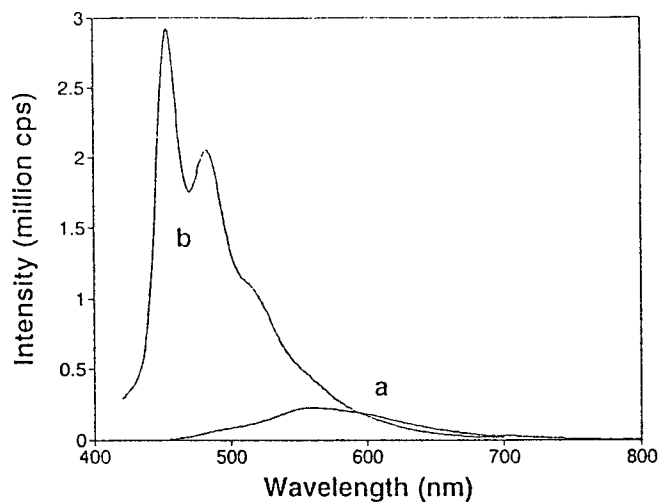
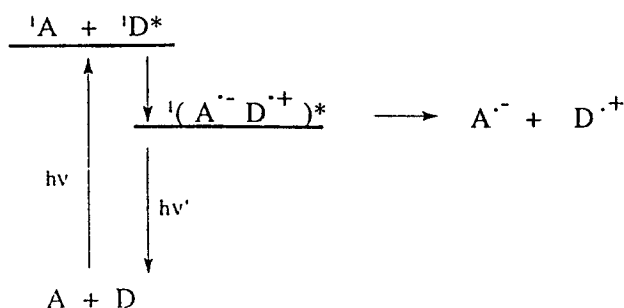


Figure 1. PL emission spectra: (a) PPyBT thin film ($\lambda_{ex} = 440$ nm); (b) thin film of PPyBT blend ($\sim 10^{-3}$ mol%, $\lambda_{ex} = 400$ nm).

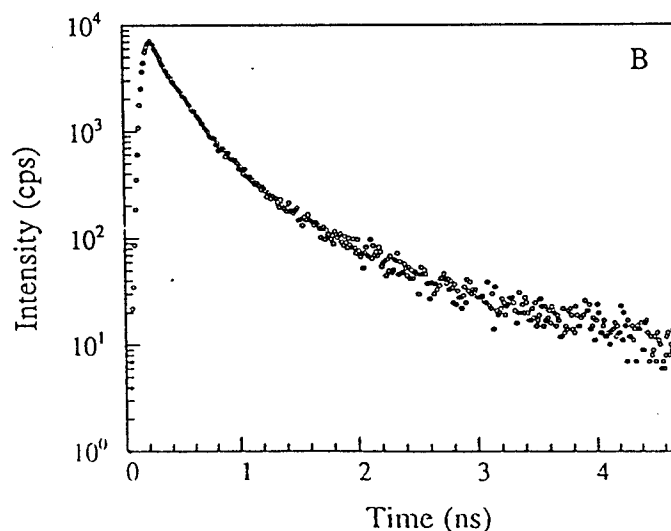


Figure 2. PL decay dynamics of PBO thin film emission at 500 nm ($\lambda_{ex} = 380$ nm).